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REDOX POTENTIAL OF A GLASS MASS WHEN USING OFF-GRADE RAW MATERIALS

K. V. Goncharov[1]

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The redox conditions for glass making are investigated on a working glass-melting furnace using molding sand. Data obtained from instrumental measurements of the ROP of the glass mass and reasons for destabilization of the technological process are presented.

An important factor affecting the efficiency of glass making is the ROP index of the glass mass. This index characterizes the course of the redox processes in the glass mass and is determined by the presence of oxidizers and reducers in the raw materials used for and the composition and method of preparing the batch as well as the technological regime for making glass.

The redox interaction processes in a glass mass have been elucidated in the last few years [1 – 6].

In the references cited at the end of this article, the effect of the ROP on the tint of the glass mass and the corrosion of the electrodes and refractories were investigated and the effect of introducing melting accelerators, the chemical composition of borosilicate glasses, the melting temperature, and the type of raw materials used were determined according to how they affect the redox equilibrium Fe(II) ⇄ Fe(III). The indicator $d_{Fe(II)}$ and the redox factor (which indicates the state of the $FeO : Fe_2O_3$ equilibrium) were used to evaluate the ROP of the glass mass [2].

Analysis of the operation of the glass making and production system at the Irbit Glass Works shows that by influencing the ROP of the glass mass it is possible to use internal reserves to increase the capacity of the glass-making furnace even using raw materials which were never intended for glass making [7].

Laboratory investigations have established that the redox conditions of glass melting, which in turn depend on the presence of iron and chromium impurities in the raw materials, have the greatest effect on the FeO content and the ratio $FeO : Fe_2O_3$.

The redox state of the raw materials and batch can be calculated and the ROP can be determined analytically by well-known methods.

A quantitative evaluation of the ROP of a batch (glass mass) was made under laboratory conditions by a method based on the potassium permanganate oxidation of reducers which are components of the daily average sample of the batch followed by titration of the excess potassium permanganate using ferrous ammonium sulfate. The optimal chemical oxygen utilization (COU) index was established to be from – 4 to – 15 mg O_2, which corresponds to the optimal amount of FeO — 0.0182 – 0.0195% and the optimal ratio $FeO : Fe_2O_3 = 25 – 27$ with the total iron content in the glass mass 0.120 – 0.125%. The ratio of the iron oxides converted to the metal ratio Fe(III) : Fe(II) was also used as an indicator of the state of the $FeO \rightleftarrows Fe_2O_3$ equilibrium and the ROP of the glass mass.

It is well known that glass does not have a strict, ordered structure. As molten glass cools it gradually passes into a solid state and its properties — the viscosity, density, stresses, CLTE, and others — change abruptly. Glass with the same chemical composition can have different technological properties. For this reason, the properties of final glass product are determined not only by the chemical composition but also by the recent thermal (temperature) history of the melt and the redox conditions of glass melting.

Heat transfer into the deep interior layers of a glass-mass in the melting tank occurs by radiation from a flame (radiative heat conduction). The contribution of the radiation mechanism of heat transfer becomes especially important in the zone of high (maximum) melting temperatures. Consequently, a glass mass with a high FeO content transfers heat poorly into the deep interior layers (near the bottom), as a result of which the top layers become overheated and the bottom layers are chilled.

Radiative heat conduction is essentially independent of the chemical composition of the glass. It depends mostly on

[1] Irbit Glass Works LLC, Irbit, Russia.

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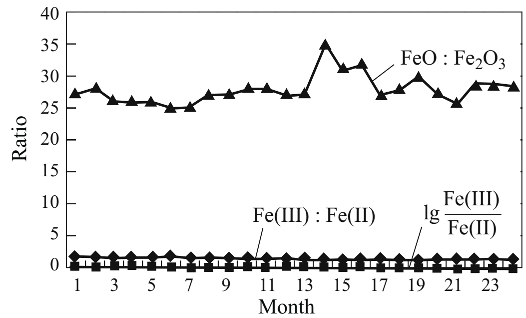

Fig. 1. Data on the evaluation of the ROP of a glass mass for the years 2005 and 2006. Content over one year (%): 0.123 and 0.123 Fe_2O_3 (total), 0.0189 and 0.0197 FeO, 27 and 29 (FeO : Fe_2O_3), respectively.

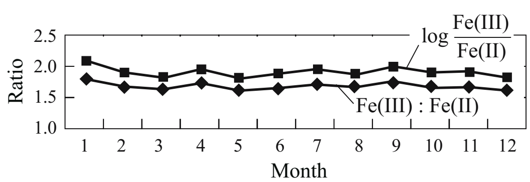

Fig. 2. Data on evaluation of the ROP of a glass mass over the year 2000. Content over the year (%): 0.155 Fe_2O_3 (total), 0.025 FeO, 26 (FeO : Fe_2O_3).

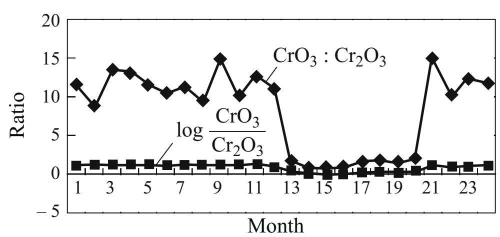

Fig. 3. Data on the evaluation of the oxygen potential or ROP of glass mass over the years 2005 – 2006.

the FeO content and the ratio FeO : Fe_2O_3, which characterize the ROP of the glass mass.

A convective back flow from the zone of maximum temperatures transfers heat under the batch. The enthalpy of the glass mass flow can be increased by creating the optimal diathermancy of the melt, which is evaluated via the FeO content and the ratio FeO : Fe_2O_3. If the temperature in the bottom layers of the melt in the zone of maximum temperatures and under the batch in the zone of the first few pairs of burners (loading well) decreases with the fuel feed rate remaining constant, then measures must be taken, first and foremost, to optimize the FeO content.

The thermal regime of a tank furnace changes for many reasons. Fluctuations of the thermal regime disrupt the character of the exchange of the glass mass in the tank and disrupt the stability of the established flows of the glass mass. In turn, a change in the enthalpy of the melt causes stagnant layers of the glass mass to be drawn into the output (working) flow (if diathermancy increases) or promotes the formation of an undesirable temperature gradient (if diathermancy decreases) and chills the bottom layers of the glass mass in the tank and, in consequence, decreases the chemical and thermal nonuniformity of the glass mass, decreases the output, and degrades the quality of the finished glass.

Figure 1 displays comparative data from measurements of the ROP of a glass mass performed over the period 2005 – 2006 with essentially the same total iron content but with different and unstable ratios of the forms of iron and chromium with different valence, expressed in terms of the oxides and in terms of the metal itself. But, for optimal diathermancy and ROP of the glass mass the glass melting and production regime is stable even with high, unstable, total iron content (Fig. 2). These data confirm that the operational stability of the glass melting and production system depends on holding the optimal value of the ROP of the glass mass even when off-grade raw materials are used.

In the presence of redox forms of iron and chromium oxides the process of establishing equilibrium between the oxides with different valence is determined by oxygen diffusion in the molten glass. Oxygen diffusion has a large effect on the process of melting and forming glass.

Laboratory investigations of the effect of the ROP on the operation of the glass melting and production system were performed on a working glass-making tank furnace. The content of chromium oxides with different valence as an indicator of the oxygen saturation of the glass mass was also determined. To evaluate the oxygen potential of the glass mass the content of Cr_2O_3 and CrO_3 was measured using a method developed in the laboratory. The changes in the content of chromium with different valence in the glass mass were followed, and the oxygen partial pressure in the glass melt was determined.

In a glass melt, Cr(VI), being a strong oxidizer, promotes oxidation of Fe(II) to Fe(III) and also, for example, conversion of the forms of iron and chromium with different valence according to the scheme

$$\mathrm{Cr(VI) + Fe(II) \rightleftarrows Cr(III) + Fe(III);}$$
$$\mathrm{Cr(III) \rightleftarrows Cr(VI).}$$

Since the forms of chromium with different valence which come together with the sand are present in the glass mass, it was necessary to confirm that the ratio $CrO_3 : Cr_2O_3$ also affects the FeO $\rightleftarrows$ Fe_2O_3 equilibrium (Fig. 3).

The $CrO_3 : Cr_2O_3$ ratio found was used as an indicator of oxygen saturation of the glass mass. This indicator also characterizes the redox conditions in the glass mass. In Figs. 2 and 3, the changes in the ROP and in the oxygen potential of the glass mass have the same character.

The results obtained with the glass melting and production system over the last 12 years confirm that the efficiency of the glass-making process largely depends on the redox conditions of melting.

In summary, investigations performed over many years and analysis of the operation of a glass melting and production system have established the reasons for the destabilization of the process of melting and producing glass. The following conclusions have been drawn:

the ROP of a glass mass largely determines the content of oxidizers and reducers in the batch; to maintain a constant ROP, which is determined via the COU, the amounts of reducers and oxidizers must be monitored and the batch composition has to be adjusted when they exceed the admissible levels;

analytical determination of the COU of a batch at the batch preparation stage makes it possible to control the glass making process and the properties of the melt, such as the diathermancy and quality, which permits a complete evaluation of the technological and final properties of the glass mass;

the equilibria $Cr(III) \rightleftarrows Cr(VI)$ and $Fe(II) \rightleftarrows Fe(III)$ depend on the oxygen potential of the glass mass, expressed by the of the partial pressure indicator for oxygen with which the glass mass is in equilibrium.

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